Fluorine and chlorine fractionation during magma ocean solidification: Implications for the origin and abundance of terrestrial halogens

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The isotopic compositions of terrestrial volatiles, such as hydrogen, nitrogen, and chlorine, are very similar to that of volatile-rich CI-CM type carbonaceous chondrites [e.g, 1, 2], suggesting that terrestrial volatile elements may have been mainly derived from these types of asteroids during the formation of the Earth. However, the abundance pattern of volatiles in the silicate Earth is different from carbonaceous chondrites [e.g., 1]. More specifically, super-chondritic H/N, Ar/Xe, and F/Cl ratios of the Earth have been reported [e.g., 1]. The simplest explanation for these observations is that terrestrial volatiles were delivered and fractionated during the main accretion phase. If this is the case, elucidating the fractional processes of volatiles in terrestrial planets is a key to understanding the origin of volatiles in terrestrial planets.

In this study, we focus on the super-chondritic F/Cl ratio of the Earth. The super-chondritic F/Cl ratio of the Earth indicates the selective loss of chlorine and the preferential retention of fluorine. Previous experimental studies have shown that fluorine and chlorine are moderately to highly lithophile under high pressure and high temperature conditions [3, 4, 5]. This indicates that fluorine and chlorine would have been partitioned into mantle during core-mantle separation. Thus, fluorine and chlorine fractionation would have occurred during magma ocean solidification and/or subsequent degassing processes. In order to test the former case, we experimentally investigate the solubility of fluorine and chlorine in mantle minerals at the transition zone and lower mantle conditions.

Starting materials were composed of high-purity oxides (SiO_2, Al_2O_3, CaO, MgO, FeO) and iron metal (Fe) with enstatite chondritic proportion [e.g., 6]. Fluorine and chlorine were added to the mixture as CaF_2 and $FeCl_2$, respectively. The starting materials were encapsulated into a graphite capsule. The experiments were performed at 18-25 GPa and 2123-2273 K using the multi-anvil press at Ehime University. The elemental compositions and phase assemblies of recovered samples were determined by raman spectroscopy, microfocused X-ray diffractometry, and electron microprobe analyzer. The abundances of fluorine and chlorine in minerals were determined by nano-scale secondary ion mass spectrometry at Atmosphere and Ocean Research Institute.

The preliminary experimental results show that the solubility of fluorine in $MgSiO_3$ majorite is approximately one order of magnitude higher than that of chlorine. Although we did not investigate the mineral-melt partition coefficients for fluorine and chlorine, the experimental results show that the crystallization of majorite in a deep magma ocean might have increased F/Cl ratios of the solid mantle. If the compatibility of fluorine and chlorine with other mantle minerals is similar to the case of majorite, the degassing of volatiles with high F/Cl ratios from the mantle after the escape of chlorine-rich primordial atmospheres might have yielded the current abundance pattern of terrestrial halogens. This hypothesis is consistent with the recent proposed scenario for explaining terrestrial super-chondritic Ar/Xe ratio [7].

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Keywords: Halogen, Magma ocean

Volatile element transport within a closed system constrained by halogens and noble gases in mantle wedge peridotites

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Halogen and noble gas systematics are powerful tracers of volatile recycling in subduction zones. The presence of noble gases and halogens with seawater and sedimentary pore-fluid signatures in exhumed mantle wedge peridotites and eclogites from the Sanbagawa-metamorphic belt, southwest Japan [1,2], and in seafloor and forearc serpentinites [3] along with seawater-like heavy noble gases (Ar, Kr, and Xe) in the convecting mantle [4] strongly suggest the subduction of sedimentary-pore-fluid-like noble gases and halogens.

In order to determine how volatiles are carried into the mantle wedge and how the subducted fluids modify halogen and noble gas compositions in the mantle, we analyzed halogen and noble gas compositions of mantle peridotites containing H_2O-rich fluid inclusions collected at volcanic fronts from two contrasting subduction zones (the Avacha volcano of Kamchatka arc and the Pinatubo volcano of Luzon arcs) and orogenic peridotites from a peridotite massif (the Horoman massif, Hokkaido, Japan) which represents an exhumed portion of the mantle wedge [5].

The halogen and noble gas signatures in the H_2O-rich fluids are similar to those of marine sedimentary pore fluids and forearc and seafloor serpentinites. This suggests that marine pore fluids in deep-sea sediments are carried by serpentine and supplied to the mantle wedge, preserving their original halogen and noble gas compositions.

On the other hand, the measured Cl/H_2O and $^{36}Ar/H_2O$ in the peridotites are higher than those in sedimentary pore fluids and serpentine in oceanic plates. The halogen/noble gas/H_2O systematics are interpreted within a model where water is incorporated into serpentine in a closed system formed along fracture zones developed at the outer rise, where oceanic plates bend prior to entering subduction zones, preserving Cl/H_2O and $^{36}Ar/H_2O$ values of sedimentary pore fluids. Dehydration–hydration process within the oceanic lithospheric mantle maintains the closed system until the final stage of serpentine dehydration. The sedimentary pore fluid-like halogen and noble gas signatures in fluids released at the final stage of serpentine dehydration are preserved due to highly channelized flow, whereas the original Cl/H_2O and $^{36}Ar/H_2O$ ratios are fractionated by the higher incompatibility of halogens and noble gases in hydrous minerals. The fluids are supplied to the mantle wedge beneath volcanic fronts and trapped as fluid inclusions in mantle wedge peridotites.

Some studies have argued that the sources of trace elements and water are decoupled in subduction zone magmas and that the major source of water is serpentine. Halogen and noble gas signatures found in the peridotites investigated here reveal that serpentine supplies a significant amount of water to the mantle wedge beneath volcanic fronts, and that this water is not strongly decoupled from these two groups of elements. The seawater-like noble gases in the convecting mantle [4] can be also explained by deeper subduction and/or involvement of the noble gas signatures observed in this study, to the convecting mantle.

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Keywords: halogen, noble gas, mantle, subduction, slab fluids

Systematics of volatile elements in melt inclusions from the proto-Izu-Bonin-Mariana arc (30-40 Ma)

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IODP Expedition 351 “Izu-Bonin-Mariana (IBM) Arc Origins” drilled at Site U1438 in the Amami Sankaku Basin, about 100 km west of the Kyushu-Palau Ridge, a remnant of the IBM arc. We recovered 1611-m-long cores composed of 150-m of igneous basement (Unit 1), which were formed when subduction initiated at ~52 Ma, and 1461-m of sediments (Units I, II, III and IV), which were deposited immediately after subduction initiation (Fig. **a**). We focused on Unit III (30-40 Ma) and have already analyzed the major elements and volatile elements (S and Cl) of more than 300 melt inclusions from Unit III with electron probe microanalyzers and have discussed the causes for temporal changes in volcanism of the proto-IBM arc (Brandl et al., 2017; Hamada et al., under review).

In order to extend our previous studies, we analyzed the concentrations of four volatile elements (H_2O, S, Cl, F) and P_2O_5 of a sub-set of 56 representative melt inclusions by Secondary Ion Mass Spectrometry (SIMS) at the Kochi Institute for Core Sample Research of JAMSTEC. Quantification of volatile elements was based on callibration lines and volatile standards by Shimizu et al. (2017). Generally, abundances of volatile elements increase from 40 Ma to 30 Ma (Figs. **b-e**), along with incompatible elements such as K_2O and P_2O_5 (Fig. **f**). As a result, the ratios of volatile elements to incompatible elements, such as F/K_2O and Cl/K_2O, are almost constant from 40 Ma to 30 Ma, irrespective of the rock series (low-K series or medium-K series) and chemical groups (clusters) of melt inclusions assigned by Hamada et al. (under review) (Figs. **g** and **h**). Because frontal-arc volcanoes and rear-arc volcanoes of the IBM arc are characterized by low-K series rocks and medium-K series rocks, respectively, these results suggest that (i) the volcaniclastics that accumulated at Site U1438 originate from both frontal-arc volcanism and rear-arc volcanism, and that (ii) volcanism around Site U1438 shifted from frontal-arc to rear-arc volcanism over time.

Volatiles in silicic (dacitic~rhyolitic) melt inclusions (Cluster 6 melt in Figs. **g** and **h**) seem to behave differently from those dissolved in mafic melts. Fluorine concentration of silicic melt inclusions (600-800 ppm) does not increase with increasing K_2O (Fig. **g**). Silicic melt inclusions mainly occur at ~30 Ma, the upper level of Unit III, which corresponds to the timing just before the arc rifting and back-arc opening of the IBM arc from ~25 Ma. These silicic melts may be a products of fractional crystallization or may be crustal anatexis (Ikeda and Yuasa, 1989). With respect to the occurences of extremely Cl-rich melt inclusions (Cluster 2 melt inclusions in Figs. **g** and **h**), we discuss two possibilities for their origin: one is that they are the “halogen-rich andesite melts” as proposed by Straub and Layne (2003) for the IBM arc; the other is brine assimilation in a submarine hydrothermal system. No F enrichment is observed for extremely Cl-rich (Cluster 2) melt inclusions, and they cannot be “halogen-rich andesite melts” (Straub and Layne, 2003). Therefore, brine assimilation likely explains the origin of extremely Cl-rich melt inclusions.

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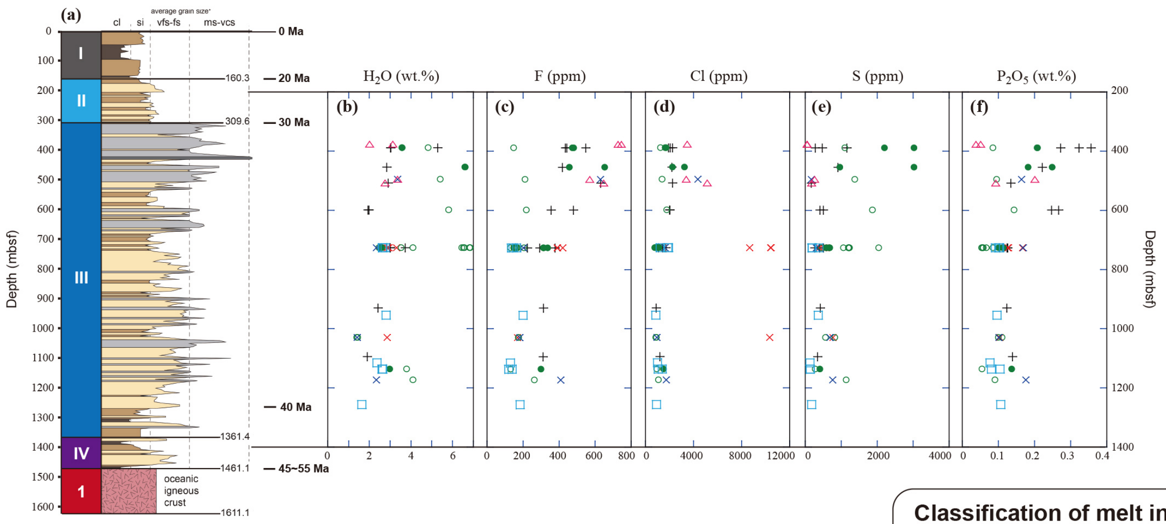
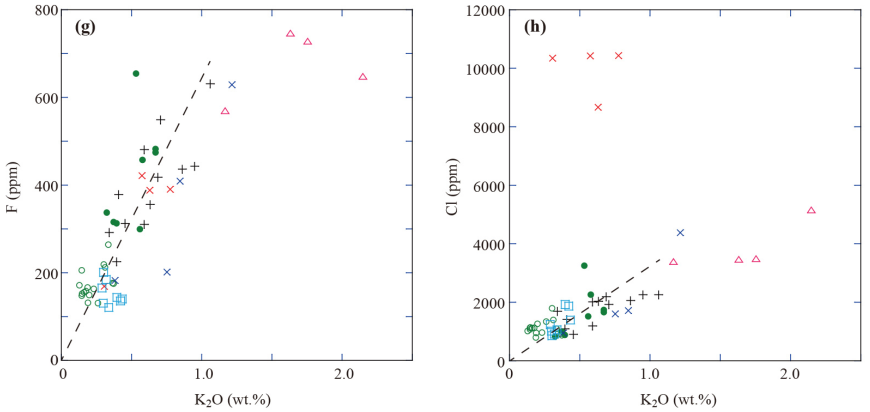
Keywords: IODP, Izu-Bonin-Mariana arc, Amami Sankaku Basin, Melt inclusion, SIMS





Classification of melt inclusions by Hamada *et al.* *(under review)*

+ **Cluster 1 melt inclusions**
(Medium-K tholeiitic series rocks)

× **Cluster 2 melt inclusions**
(Extremely high-Cl melt inclusions)

○ **Cluster 3 (low-K) melt inclusions**
(High-S melt inclusions)

● **Cluster 3 (medium-K) melt inclusions**
(High-S melt inclusions)

× **Cluster 4 melt inclusions**
(High-Cl melt inclusions)

□ **Cluster 5 melt inclusions**
(High-Mg calc-alkaline andesites)

△ **Cluster 6 melt inclusions**
(Dacitic~rhyolitic melt inclusions)

Fluid-fluxed melting of the mantle as the cause of intraplate magmatism over a stagnant slab: implications from Fukue Volcano Group, SW Japan

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The Pacific Plate subducting from the Japan Trench has accumulated in the mantle transition zone beneath NE Asia, and intraplate magmatism has been active above the stagnant Pacific slab. Since the discovery of a remnant of the Pacific slab in the mantle transition zone (Fukao et al., 1992), slab stagnation and its relationship with intraplate magmatism has received growing attention. In particular, electric conductivity observations have suggested a remarkably hydrous mantle transition zone beneath NE China (e.g., Kelbert et al., 2009), and experimental, seismic, and numerical studies have indicated that dehydration of the stagnant slab plays a significant role in magma genesis (e.g., Ohtani and Zhao, 2009). In this study, a petrological and geochemical study was carried out on basalts from a monogenetic volcano (Akashima Volcano) in the Fukue Volcano Group, SW Japan, to clarify the role of deep dehydration of the stagnant Pacific slab in the magmatism.

Akashima is a small volcanic island (0.52 km^2), located southeast of Fukue Island, which is at the southwestern end of the Goto Islands. The eruption products (46.8–51.0 wt.% SiO_2) consist of a low-Si group (< 48.4 wt.%) and a high-Si group (> 48.8 wt.%), and the former predates the latter. The modal abundance of phenocrysts is typically ˜5% olivine for the low-Si group. Some samples additionally contain small amounts (< 0.5%) of plagioclase phenocrysts. The products of the high-Si group typically contain ˜5% olivine and ˜10% plagioclase phenocrysts. The low-Si samples have higher TiO_2 and rare-earth element concentrations, and higher $^{87}Sr/^{86}Sr$ ratios and lower $^{143}Nd/^{144}Nd$ and $^{206}Pb/^{204}Pb$ ratios than the high-Si samples.

The low-Si samples have distinct incompatible element concentrations and Sr, Nd, and Pb isotopic compositions from those of the high-Si samples. This observation suggests that the low-Si and high-Si magmas were not produced by a series of magmatic processes. The most magnesian samples in each group are primitive (> 8 wt.% MgO), and therefore, both the low-Si and high-Si magmas originated from different source mantle materials. The H_2O contents of the primary magmas were estimated as ˜2 wt.% for both the low-Si and high-Si groups. Analyses using multicomponent thermodynamics suggested that the low-Si and high-Si primary magmas were generated at ˜2.5 GPa and 1345ºC and at ˜1.8 GPa and 1285ºC, respectively. The melting pressure of ˜2.5 GPa for the low-Si magma suggests its generation in the asthenospheric mantle. On the other hand, the melting pressure of ˜1.8 GPa for the high-Si magma coincides well with the depth of the asthenosphere–lithosphere boundary at 60–65 km (˜1.8 GPa) beneath Fukue Island (Zhu et al., 2006). Therefore, the high-Si magma is considered to have been generated by interaction of the low-Si magma with the SCLM.

The H_2O/Ce ratios of the primary low-Si magma of ˜650 is higher than the range of 100–250 for normal MORB (Michael, 1995), and is closer to the range found in subduction zone magmas (800–10000; Ruscitto et al., 2012). This observation suggests that the source mantle of the Akashima magma is

significantly hydrous compared with the normal asthenospheric mantle. The mantle potential temperature for the low-Si Akashima magma, calculated as ˜1300ºC, is within the range for subduction zone magmas (1150–1350ºC; Lee et al., 2009). Therefore, the Akashima magma may have been generated primarily by melting of the ambient asthenospheric mantle at ˜2.5 GPa, triggered by an influx of fluids originating from dehydration of the stagnant Pacific slab, similar to the case of the Chugaryong Volcano in Korea (Sakuyama et al., 2014). The water storage capacity of the upper mantle is significantly lower than that of the underlying mantle transition zone. Therefore, the release of fluids from the mantle transition zone to the upper mantle may suggest that the transition zone beneath Akashima was locally saturated with water.

Keywords: Intraplate magmatism, Mantle transition zone, Water, Stagnant slab

Temporal variation of He isotopes in fumarolic gases at Mt. Hakone, Japan

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Volcanic and seismic activity was intensified at Mt. Hakone in 2015. Earthquake swarm activity was observed in the end of April 2015, which was followed by small eruptions at the Owakudani geothermal area from June to July. Eruptions and seismic activity had been frequently observed till about October 2015, and the activity became calm in the end of the year. From May 2015, we have been investigating $^{3}He/^{4}He$ ratios in fumarolic gases collected at two sites in the Owakudani geothermal area, located at Mt. Kamiyama which is one of the central cones of Hakone caldera. One fumarolic gas (T) is located near the parking of the geothermal area, and another fumarolic gas (S) is located on the north flank of Mt. Kamiyama, 500m far from the fumarole T. Helium isotopes in collected gases were measured with Helix-SFT or VG5400 mass spectrometer housed at Atmosphere and Ocean Research Institute. $^{3}He/^{4}He$ ratios in samples were calibrated against atmospheric value (R_a: $^{3}He/^{4}He = 1.38x10^{-6}$). Since He isotopes are useful magmatic fluid tracers, temporal variations of $^{3}He/^{4}He$ ratios may provide information about volcanic activity. $^{3}He/^{4}He$ ratios at two fumaroles slightly increased until August 2015, also after the small eruptions from June to July. The corrected $^{3}He/^{4}He$ ratio at the fumarole T increased from 6.53 R_a (June) to 6.72 R_a (August), while that of the fumarole S increased from 6.57 R_a (May) to 6.76 R_a (August) in 2015. After that, the ratios at two fumaroles started to decrease. Corrected $^{3}He/^{4}He$ ratios at fumarole T and S decreased to 6.37 R_a (October 2016) and 6.45 R_a (September 2016), respectively. These variations may reflect hydro-volcanic activity at Mt. Hakone. At Mt. Ontake, the magmatic high He isotopic ratio was supplied into geothermal systems associated with excess water vapor which could have provided the driving force for the 2014 eruption (Sano et al., 2015). There is a possibility that elevation of He isotopic ratios may be related to vapor accumulation and potential activation of Mt. Hakone, while decrease in the ratios may reflect inactivation. We will also present N and Ar isotope data, and discuss gas geochemistry along the volcanic activity of Mt. Hakone.

Keywords: Mt. Hakone, Volcanic gas, Helium isotope

Geochemistry of olivine melt inclusions in Pitcairn Island basalts: A multiple-instrument approach

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Ocean island basalts (OIBs) provide essential information on evolution of the Earth’ s mantle, because OIBs are sourced from plumes from the deep mantle that include recycling materials. OIBs at the Pitcairn Island show distinct geochemical characteristics from other OIBs with their enriched isotopic signatures, so called enriched mantle 1 (EM1) component. This particular feature could have been caused by the involvement of recycled materials including chemically differentiated oceanic plate slab or delaminated continental lithosphere and lower crust (e.g., Eisele et al., 2002). In order to understand behavior of volatile elements during mantle recycling, we analyzed H_2O, CO_2, F, S, and Cl in the olivine-hosted melt inclusions in the Pitcairn OIBs using a secondary ion mass spectrometry (SIMS). Major and trace elements, and Pb isotope compositions were also determined on the same melt inclusions with an electron probe micro analyzer (EPMA) and a laser ablation-inductively coupled plasma-mass spectrometer (LA-ICP-MS). Most of the olivine-hosted melt inclusions contain microcrystals due to slow cooling after emplacement of the host lavas. In the preliminary study, we found that measured element concentrations were blurred by the microcrystals. Therefore, we homogenized the melt inclusions by a heating and quenching method. Homogenization experiment was performed in a $CO_2 + H_2$ atmosphere using an electric furnace. For the first step, liquidus temperature of the melt inclusions was explored by altering the furnace temperature at every 25 ˚C between 1100 ˚C and 1350 ˚C. We found that the liquidus temperature was between 1150 ˚C and 1175 ˚C. All the olivines were then heated just above the liquidus temperature at 1150 ˚C or 1175 ˚C for 10 minutes and quenched. Previous studies showed that H_2O may be diffused out from a melt inclusion through host olivine during homogenization. In order to assess the effect on H_2O diffusion, we also heated naturally homogeneous melt inclusions in a pyroclastic rock and compared H_2O concentrations before and after heating. In this presentation, effects of homogenization on volatile compositions will be discussed. After corrections for the effects of post-entrapment crystallization, concentrations of the volatile elements together with the major and trace elements, and Pb isotopes in the melt inclusions are used to explore volatile contents in the source mantle of the Pitcairn OIBs.

Volatiles in olivine-hosted melt inclusions in HIMU basalts from Raivavae, South Pacific

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Volatile cycle in the mantle has been poorly constrained because of limited number of studies thus far on volatile compositions in the mantle-derived ocean island basalts. We performed in-situ geochemical analyses on the olivine-hosted melt inclusions (MI) from Raivavae Island in the South Pacific. MIs were homogenized on the heating stage before chemical analyses. Compositions of major elements, trace elements, volatile elements, and Pb isotopes were determined by the combination of analytical techniques using EPMA, LA-ICP-MS, and SIMS. Carbon dioxide is distributed in both glasses and shrinkage bubbles in MI. We measured CO_2 density in bubbles using micro Raman spectrometry and determined the volume ratio between bubbles and MI applying micro X-ray CT technique to calculate CO_2 in bubbles, which is added to CO_2 in glasses measured with SIMS to determine the total CO_2 in MI.
The basalts from Raivavae are classified into two groups in terms of Pb isotopes. Most MI in less radiogenic-Pb basalts have similar Pb isotopic compositions to host basalts. MI in radiogenic-Pb basalts generally exhibit radiogenic (HIMU) character, but they show larger isotopic variation than the host basalts. It is notable that small number of MI have different Pb isotope ratios from host basalts, suggesting mingling of radiogenic melts and less radiogenic melts during olivine crystallization. Despite some exceptions, MI with radiogenic Pb isotopes are characterized by lower SiO_2 and higher CaO, La/Yb, and Nd/Hf than MI with less radiogenic Pb. These facts suggest that the radiogenic-Pb (HIMU) melts were formed by low-degree partial melting of carbonated source. MI with radiogenic Pb clearly show elevated Cl/Nb and F/Nd relative to MI with less radiogenic Pb. Enrichment of Cl and F in radiogenic-Pb melts implies that these elements have been transported into the mantle via subduction of hydrothermally altered oceanic crusts. The correlation of H_2O/Ce and CO_2/Nb with Pb isotopes is somewhat blurred, probably owing to degassing and diffusive loss of CO_2 and H_2O. However, MI with the most radiogenic Pb have the lowest H_2O/Ce and the highest CO_2/Nb, which may also reflect the feature of the basalt source.

Keywords: Volatile, Ocean island basalts, Melt inclusion

Determination of water content of natural talc: application to a recipe for hydrogen manometry

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Hydrogen manometry is a conventional yet powerful, absolute technique for the determinations of water contents of rocks and minerals. The concentration of water in a stoichiometric pure talc was determined by the hydrogen manometry technique so that accuracy of this technique was assessed. The talc sample was from Haicheng mine, China. Bulk chemical composition of the talc sample is ($Mg_{2.930}$, $Fe_{0.001}$) ($Si_{4.003}$, $Al_{0.002}$) on the anhydrous 11 oxygen basis (Matsumura Sangyo Co., Ltd., pers. comm.), which is nearly identical to that of the ideal talc $Mg_3Si_4O_{10}(OH)_2$. Powder X-ray diffraction also shows that the sample consists thoroughly of talc, free from any possible impurity.

About 20 mg of the <38um size fraction of the talc sample was loaded in a Pt crucible and sealed in a quartz-glass reaction vessel. The reaction vessel was then connected to a high vacuum line, and the Pt crucible was heated to 1000 ˚C at the rate of ˜1 ˚C/sec using an induction furnace to let the talc sample completely degassed. Degassing was monitored with a Pirani gauge. Degassing from the talc started at around 500 ˚C and ended by 800 ˚C. During the degassing, the released gas was continuously sublimated using liquid nitrogen, so that the gas pressure buildup in the vacuum line was kept not to exceed 10 Pa. The H_2O was cryogenically purified using an acetone - solid CO_2 mixture slurry, and then converted to H_2 gas in a deleted uranium furnace at 700 ˚C. The H_2 gas was transferred into a calibrated volume with a Toepler pump, and the pressure of the H_2 gas was determined. Complete thermal decomposition of the talc to enstatite + amorphous silica was confirmed by X-ray diffraction of the residue after degassing. Repeated measurements of the talc sample yielded H_2O content of 4.71 ±0.05 wt%. This value agrees with 4.75 wt% H_2O of the ideal talc $Mg_3Si_4O_{10}(OH)_2$ within analytical uncertainty.

The gas pressure buildup in the vacuum line could reach an order of kilopascal (one hundred times more than that in the present study) if the released H_2O gas was not continuously sublimed during the degassing process. Clog et al. (2012; Geochim. Cosmochim. Acta 83, 125-137) showed that at high temperatures under such high H_2O gas pressure, a large fraction of the H_2O gas (up to 20%) is retained in the coexisting Pt alloy, which results in a poor yield of the gas in the hydrogen manometry. Diffusion flux of H_2O (H) into Pt metal is proportional to square root of the pressure of surrounding H_2O gas. Results of the present study suggest that holding H_2O gas pressure at less than 10 Pa is a key to have accurate data from the hydrogen manometry.

Keywords: water, hydrogen manometry, talc